REVIEW

COMPOSITION AND CONTRIBUTION OF MAJOR ANTIOXIDANTS OF SELECTED CEREALS TO THEIR NUTRITION QUALITY*

J. Lachman[1], I. Capouchová[2]

Czech University of Agriculture, Faculty of Agrobiology, Food and Natural Resources, [1]Department of Chemistry, [2]Department of Plant Production, Prague, Czech Republic

Cereals are recognized as a good source of potentially health-enhancing antioxidants such as phenolics, tocopherols and carotenoids. Major antioxidants contained in cereals are polyphenolic compounds, esp. phenolcarboxylic acids, coumarins, flavonoids and anthocyanins. In the article antioxidant activity in relation to the qualitative and quantitative composition of main antioxidants, esp. phenolics in cereals and the effect of the variety and growing conditions, on their content are discussed. Differences among individual selected cereals in composition and content of different antioxidant compounds are overviewed as well.

cereal antioxidants; polyphenols; tocopherols; carotenoids

INTRODUCTION

Natural antioxidants contained in food and other biological materials have received in recent time a considerable interest because of their safety and potential nutritional and therapeutic effects. Antioxidants regarding their chemical structure could be divided into polyphenols (mainly flavonoids, anthocyanins, phenolcarboxylic acids, and coumarins), carotenoids (carotenes – precursors of vitamin A and xanthophylls), and tocopherols (vitamin E). Ascorbic acid (vitamin C) and selenium possess also a strong antioxidant activity. Antioxidants can scavenge free radicals or prevent oxidative damage from spreading out. Antioxidants can help to prevent heart diseases and cancer (Reddy et al., 2000), reduce blood pressure and harmful LDL-cholesterol (Czerwinski et al., 2004) and slow the effects of aging. These naturally occurring compounds protect the body from harmful, excess free radicals, sweeping them up before they can cause damage. Vegetables and crops are significant sources of antioxidants in human nutrition either in direct consumption or in the form of vegetable juices. Among usually consumed crops whole-grain cereals (Slavin, 2003) and potatoes (Lachman et al., 2000) are important flavonoid antioxidant sources in human nutrition according to common used dietary patterns (Kris-Etherton et al., 2002). These beneficial effects have been attributed to the unique phytochemicals in cereals that complement those found in fruits and vegetables. Although bioactive compounds are present in virtually all plant foods, their levels could vary considerably among diets depending on the type and quantity of plant constituents in the diet. Cereals are widely consumed and are a valuable means to deliver beneficial natural antioxidants to humans (Truswell, 2002).

Antioxidant activity of cereals

As Adom and Liu (2002) determined, the total antioxidant activity of corn (of free and bound antioxidant compounds) was the highest (181 mmol ascorbic acid.kg^{-1}), in descending order followed than by wheat (76.7 mmol.kg^{-1}) and oats (74.7 mmol.kg^{-1}). High correlations between total antioxidant activity and phenolics (0.983), ferulic acid (0.974) and flavonoids (0.925) were found. Products containing wheat bran exhibited higher peroxyl radical scavenging effectiveness than those with oat bran (Martinez-Tome et al., 2004). Particularly, ferulic acid as the most abundant hydroxycinnamic acid (corn bran 3.1%) is one of the most promising phenolic antioxidant (Mathew, Abraham, 2004). The highest average antioxidant activity expressed in Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) equivalents (TE) was found in whole grain wheat cereals (2,850 TE.100^{-1}.g^{-1} sample) > whole grain oat cereals (2,600 TE.100^{-1}.g^{-1}) > 100% whole grain bread (2,000 TE.100^{-1}.g^{-1}) > corn cereals (1,700 TE.100^{-1}.g^{-1}) and white bread (1,450 TE.100^{-1}.g^{-1}) by Miller et al. (2000). Baublis et al. (2000) indicated that

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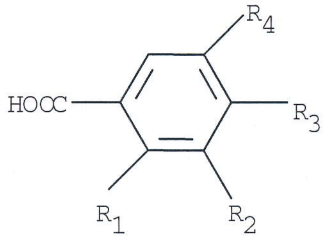
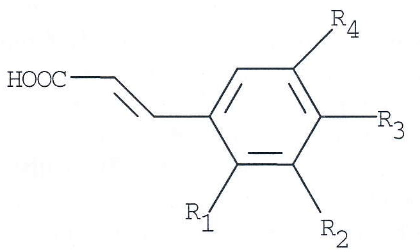
wheat-based cereals contain antioxidants whose activity is enhanced by gastrointestinal conditions suggesting that they could be important dietary antioxidants. Antioxidant activity of black sorghum was found to be very high (52–112 mmol $TE.kg^{-1}$ in grain, 190–400 mmol $TE.kg^{-1}$ in bran), as compared with cereals – buckwheat (25 mmol $TE.kg^{-1}$ in grain > barley (9–11 mmol $TE.kg^{-1}$ in grain) > rye (4 mmol $TE.kg^{-1}$ in grain) > oats (3 mmol $TE.kg^{-1}$ in grain, 5 mmol $TE.kg^{-1}$ in bran) > wheat (< 0.1–2.0 mmol $TE.kg^{-1}$ in grain, 28 – 34 mmol $TE.kg^{-1}$ in bran) (Awika et al., 2004). Whereas Perez-Jimenez and Saura-Calixto (2005) ascribe important antioxidant capacities to the fraction of nonextractable polyphenols and assume that they may have an antioxidant role in the gastrointestinal tract after colonic fermentation, Zhao et al. (2005) revealed that ferulic acid and esp. diferulic acids in cereal bran rather limit the bioavailabilities of phenolic acids in vivo. The antioxidant activity is higher for the internal bran fraction and increases in fractions having reduced granulometry (Esposito et al., 2005).

Polyphenols in cereals

There are more than 8,000 phenolic structures that have been identified till the present time, which vary from simple molecules of phenolic acids derived from benzoic and cinnamic acids to highly polymerised tannins. The flavonoids are the most common polyphenolic compounds present in plants and they could be categorized into 13 classes comprising more than 5,000 structures either in the form of glycosides or aglycones. The primary phenols in cereals are flavonoids, phenolic acids, and tannins (total content 0.7–1.6 $g.kg^{-1}$). The major polyphenolic compounds were isolated and identified from barley and triticale grains and compared with the phenolic constituents that had been found in the wheat, oat and the rye (Lachman et al., 1991, 2003). Special attention is paid to the constituents of the buckwheat as the source of rutin in human nutrition (Holasová et al., 2002). *O*- and *C*- glycosides of flavones are characteristic for cereals, esp. that derived from apigenin and luteolin. In rye and triticale have been likewise described glycosides of quercetin. Also the composition of polyphenolic complex of barley seeds indicated their strong antioxidant activity (Maillard et al., 1996). Depending on the variety, the antioxidant activity of barley is in relationship with the content of three main phenolic groups – flavan-3-ols (more than 85%), hydroxycinnamic acids (approx. 10%) and flavones (less than 5% from the total content of polyphenols). In the barley seeds antioxidant efficiency is caused mainly by flavan-3-ols and flavan-3,4-diols, resp., i.e. with gallocatechin and (-)-epicatechin and with leucoanthocyanidins of procyanidin and prodelphinidin type, which could be converted by oxidation to anthocyanidins or condense to high molecular weight phlobaphene and condensed tannin fractions. Gallocatechin could originate by the (-)-epicatechin oxidation (hydroxylation) and prodelphinidin could be formed from procyanidin. Phenolcarboxylic acids form 10% of the total polyphenol content of cereals: *p*-hydroxybenzoic acid (its hydroxylation leads to gallic acid and esterification to *m*-galloylgallic acid), vanillic acid, *o*-hydroxycinnamic acid, ferulic acid (most abundant), ferulic acid dehydromers, sinapic acid, *p*-coumaric acid, caffeic acid and chlorogenic acid are major grain constituents (Table 1, Fig. 1) (Mattila et al., 2005). For barley caryopses are typical caffeic, protocatechuic, isoferulic and vanillic acids, for oat ferulic and mandelic acids, for rye isoferulic and veratric acids and for triticale sinapic acid. Mattila et al. (2005) determined also aventhramides in three oat products (Table 2). The highest contents of total phenolic acids were in bran of wheat and rye and in whole-grain flours of these grains. Similarly the highest contents of alk(en)ylresorcinols were observed in bran of rye and wheat. Nystrom et al. (2005) investigated steryl ferulate extracts from rye and



R_3=OH, R_2=R_4=OCH_3, R_1=H syringic acid
R_3=OH, R_2=OCH_3, R_1=R_4=H vanillic acid
R_3=OH, R_1=R_2=R_4=H p-hydroxybenzoic acid
R_1=R_4=OH, R_2=R_3=H gentisic acid
R_1=OH, R_2=R_3=R_4=H salicylic acid
R_2=R_3=OH, R_1=R_4=H protocatechuic acid



R_3=OH, R_2=OCH_3, R_1=R_4=H ferulic acid
R_2=OH, R_3=OCH_3, R_1=R_4=H isoferulic acid
R_3=OH, R_1=R_2=R_4=H p-coumaric acid
R_3=OH, R_2=R_4=OCH_3, R_1=H sinapic acid
R_1=OH, R_2=R_3=R_4=H o-coumaric acid
R_2=R_3=OH, R_1=R_4=H caffeic acid

Fig. 1. Major phenolcarboxylic acids in cereals

Table 1. Major polyphenols and phenolcarboxylic acids contained in selected cereals (L a c h m a n et al., 1998)

Phenolic acids	Cereals	Polyphenol compounds	Cereals
sinapic	w, o, r	apigenin 7-*O*-rhamnoglucoside	b
ferulic	w, b, o, t	isoschaftoside, schaftoside	w
salicylic	b, r, t	6-*C*-arabinosyl-8-*C*-arabinosylapigenin	w
gentisic	r, t	apigenin 8-*C*-arabinosylhexoside	o
homogentisic	o, r, t	apigenin 8-*C*-rhamnosylglucoside	o
o-OH cinnamic	b	vitexin (8-*C*-glucosylapigenin)	bw
chlorogenic	w, b, r	isovitexin (6-*C*-glucosylapigenin)	w, b, r, bw
gallic	b	isoswertisin 4´-*O*-glucoside	w
m-galloylgallic	b	vicenin-1,2 (6,8-*C*-diglucosylapigenin)	w, b, r
protocatechuic	b	luteolin	r
caffeic	b, o, r, t	orientin (8-*C*-glucosylluteolin)	bw
hydroxycaffeic	o, r, t	isoorientin (6-*C*-glucosylluteolin)	w, b, bw
vanillic	w, b, t	2´´-*O*-glycosylisovitexin	b
m-hydroxybenzoic	b, r	lutonarin (isoorientin 7-*O*-glucoside)	w, b
mandelic	o	lucenin-1,2 (6,8-*C*-diglucosylluteolins)	w
o-coumaric	w, b, r	chrysoeriol 7-*O*-rhamnoglucoside	r
homovanillic	o	tricin	w, b, r
p-hydroxybenzoic	b, o	glucotricin	b
p-coumaric	w, b, o, t	tricinin	b, r
syringic	b	tricin 5-*O*-glucoside	r
veratric	b, o, r	isorhamnetin 3-*O*-rutinoside	r
		rutin	t, bw
Coumarins		isoquercitrin	t
umbelliferon	b	cyanidin 3-*O*-glucoside and galactoside	bw
esculetin	b	cyanidin 3-*O*-rhamnosylgalactoside	bw
scopoletin	b, t	quercetin	t, bw
herniarin	b	procyanidin	b
		(-)-epicatechin	b
		prodelphinidin	b
		gallocatechin	b

b – barley, w – wheat, o – oat, r – rye, t – triticale, bw – buckwheat

wheat bran and indicated that especially ferulic moiety was responsible for the antioxidant properties. The average total polyphenol content in barley caryopses is higher in comparison with other cereals, e.g. triticale (L a c h m a n et al., 1998, Table 2). In the group of flavonoids *O*- and *C*- glycosides of flavones are characteristic for cereals, esp. that derived from apigenin and luteolin (Fig. 2). Depending on the variety, the antioxidant activity of barley corresponds to the content of the three main phenolic groups – flavan-3-ols (more than 85%), hydroxycinnamic acids (approx. 10%) and flavones (less than 5% from the total content of polyphenol) (M a i l l a r d et al., 1996). The major antioxidant activity possess flavan-3-ols. In the barley seeds antioxidant efficiency is caused mainly by flavan-3-ols and flavan-3,4-diols (more than 85%), i.e. with gallocatechin and (-)-epicatechin and with leucoanthocyanidins of procyanidin and prodelphinidin type, which could be converted by oxidation to anthocyanidins or condense to high molecular weight phlobaphene and condensed tannin fractions. Gallocatechin could originate by the (-)-epicatechin oxidation (hydroxylation), prodelphinidin likewise from procyanidin. The average catechin, resorcin and phloroglucinol type phenol content in barley caryopses is relatively high (in the range from 95 to 448 $mg.kg^{-1}$ DM). Content of phenolics in the cereal caryopses is significantly dependent on the given variety and it is influenced by the locality, specific weather conditions of the given year and the conditions of ageing. According to data of V e l i o g l u et al. (1998), wheat germ contained 3.49 $g.kg^{-1}$ total phenolics, buckwheat seeds 7.26 and hulls 39 $g.kg^{-1}$. With increasing germination time after 7 days concentrations of ferulic and vanillic acids increased reaching 932.4 $mg.kg^{-1}$ and 12.9 $mg.kg^{-1}$, resp. (Y a n g et el., 2001). As A d o m and L i u (2002) demonstrated, there exists highly correlated

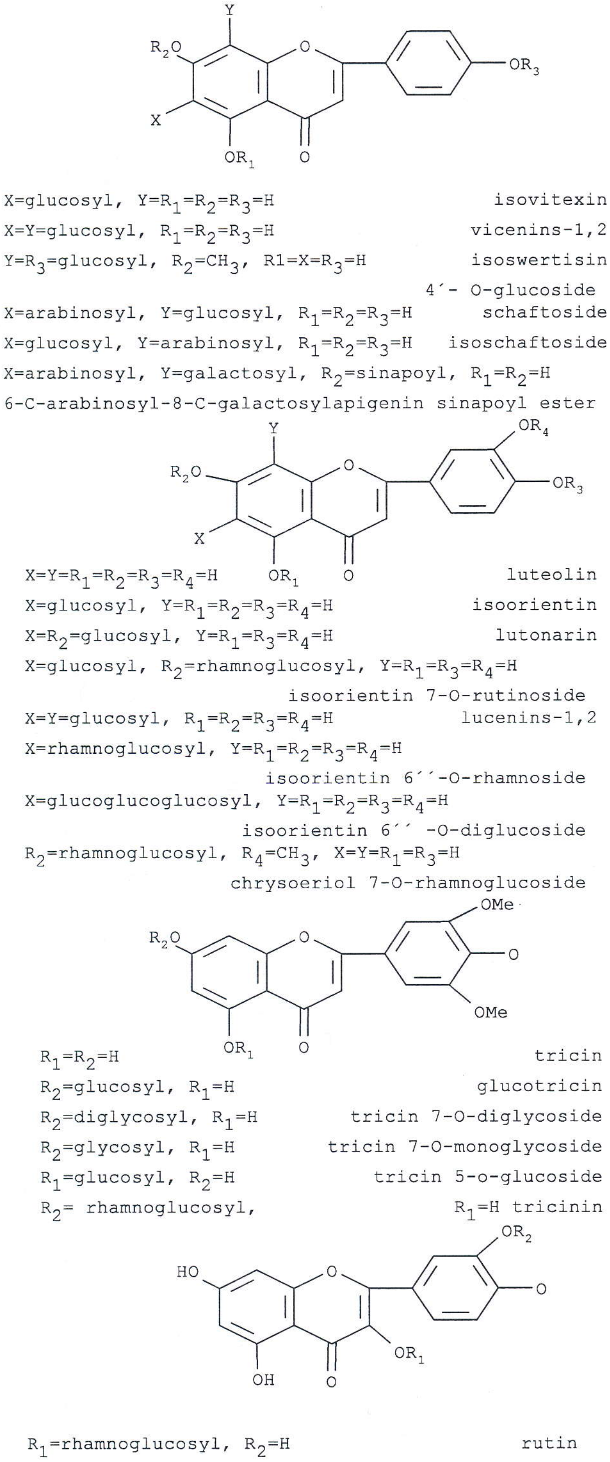


Fig. 2. Major flavonoids in cereals

bound phenolic and ferulic acid content with the total antioxidant activity ($R^2 = 0.991$, $p < 0.01$). Cereals containing a high proportion of the bran layers are rich in ester-linked hydroxycinnamic acids, such as ferulic and diferulic acids (Kern et al., 2003). Esp. diferulic acids bound as structural components of cereal cell walls are potent antioxidants (Andreasen et al., 2001), e.g. in rye (Andreasen et al., 2000) and more bioavailable than the free form (Rondini et al., 2004). From most cereal insoluble dietary fibre broad spectrum of dehydrodiferulic acids (8-5´-, 8-8´-, 5-5´-, 8-*O*-4´- and 4-*O*-5´-coupled) was identified by Bunzel et al. (2001) within range of total content between 2.4 and 12.6 g.kg^{-1}. Major dimers differ in soluble dietary fibre (8-8´ -) and insoluble fraction (8-5´-coupled dimers), often bound via glycosidic bound to α-L-arabinofuranose and β-D-xylopyranose (Rhodes et al., 2002). Zhou et al. (2004a) confirmed that ferulic acid, with a concentration range of 99–231 mg.kg^{-1}, was the predominant phenolic acid (accounted for about 46–67%) of total phenolic acids in wheat bran (5 g.kg^{-1} wheat bran, Scalbert and Williamson, 2000). Similarly, ferulic acid was the predominant antioxidant contained in red wheat (Zhou et al., 2004b). As Drankhan et al. (2003) found, the content of orthophenolic acids in wheats predicts their antitumour activity. Another source of antioxidant properties represent red and black cereal varieties, esp. sorghum varieties, accounting for about 50% of the anthocyanins, among them mainly luteolinidin and apigeninidin are contained (Awika et al., 2004). As Abdel-Aal and Hucl (2003) found, cyanidin 3-*O*-glucoside is the predominant anthocyanin contained in purple wheat. It is interesting fact that highly roasted corn and wheat products possess lower antioxidant contents than those not or less roasted samples (Hernandez-Borges et al., 2005).

Other antioxidants contained in cereals

Tocopherol and tocotrienols (tocochromanols, vitamin E) are lipophilic antioxidants mostly present in the pericarp as well as the endosperm fraction of barley caryopses (Falk et al., 2004). About 85% of the tocochromanols are tocotrienols, in the case of the tocopherols 80% are present in the germ fraction. The concentrations for α-, δ-, and γ-tocopherols in wheat bran determined Zhou et al., (2004a, Table 2). Cereals, especially oat, rye, and barley, are good sources of tocotrienols. As Panfili et al. (2003) determined, the highest tocol levels were found in barley and soft wheat. From individual compounds β-tocotrienol is the most contained in hulled and dehulled wheat, whereas γ-tocopherol predominates in corn and α-tocotrienol in oat and barley. As Gray et al. (2002) by comparison of antioxidant activity of oat extracts found, α-tocopherol and Trolox possess similar activity per mole. In oat the antioxidant complex is formed by tocols, phytic acid, phenolics, and avenanthramides, which have protective function in a plant defence response (Peterson, 2001). Among carotenoids, lutein and cryptoxanthin were determined in bran wheat samples (Zhou et al., 2004a, b). The highest content was found for zeaxanthin and β-carotene. Similarly, as in the case of ferulic and vanillic acids, also the concentrations of α-tocopherol, β-carotene and ascorbic acid increased with germination time, reaching their maxima after 7 days (Yang et al.,

Table 2. Contents of major antioxidants in cereal seeds and products

Cereal	Polyphenols	Tocopherols, tocotrienols	Carotenoids	Aventhramides	Ascorbic acid	References
Barley caryopses	860–1690[b] TP	75[b] tocol				Lachman et al. (1998)
	95–448[b] CRP	40[b] α-tocotrienol				Panfili et al. (2003)
	2000–6000[a] tyrosine	56–71[a] tocopherol	1[a] β-carotene			Duke (1992)
Buckwheat seeds	7260[a] TP	42[a] tocopherol				Velioglu et al. (1998)
	39 000[a] TP					Duke (1992)
Buckwheat hulls	2750[a] tyrosine					
Cereal insoluble dietary fibre	2400–12 600[a] dehydrodiferulic acids					Bunzel et al. (2001)
Corn seeds	6–27[a] ferulic acid	45[b] α-tocotrienol	0.5–2.5[a] α-carotene		85[a]	Panfili et al. (2003)
	1230–5117[a] tyrosine		0.5–2.5[a] β-carotene			Duke (1992)
Oat flakes				26–27[a]		Matilla et al. (2005)
Oat bran				13[a]		Panfili et al. (2003)
Oat seeds	2000–14 000[a] tyrosine	56[b] α-tocotrienol	0.22[a] total carotene			Duke (1992)
		4.4–10.1[a] α-tocopherol				
Rye bran	4190[a] PA					Matilla et al. (2005)
	4108[a] alk(en)ylresorcinol					Duke (1992)
Rye seeds	3390–3800[a] tyrosine	800[a] tocopherol				
Rye whole-grain flours	1366[a] PA					Matilla et al. (2005)
Triticale seeds	440–610[b] TP					Lachman et al. (1998)
Wheat bran	4527[a] PA	1.28–21.29[a] α-tocopherol	0.50–1.80[a] lutein			Zhou et al. (2004
	3225[a] alk(en)ylresorcinol	0.23–7.00[a] δ-tocopherol	0.18–0.64[a] cryptoxanthin			
		0.92–6.90[a] γ-tocopherol	2.19[a] zeaxanthin			
		18.7 – 29.5[c] tocopherol	0.09–0.40[a] β-carotene			Panfili et al. (2003)
	130–5000[a] FA					Matilla et al. (2005)
Wheat whole- grain flours	1342[a] PA					
			10.92[a] α-carotene			Yang et al. (2001)
			3.1[a] β-carotene		550[a]	Velioglu et al. (1998)

	3490^a TP					Panfili et al. (2003)
	$3–4^a$ caffeic acid	$59–1897^a$ tocopherol	0.22^a β-carotene			Duke (1992)
Wheat sprout seedlings	$2–4^a$ gentisic acid					
	$17–25^a$ *p*-coumaric acid	75^b tocol				
	$5–10^a$ *p*-hydroxybenzoic acid	$33–43^b$ β-tocotrienol				
Wheat seeds	$3–6^a$ protocatechuic acid					
	$3–4^a$ salicylic acid					
	$3–5^a$ syringic acid					
	$1000–9000^a$ tyrosine					
	$13–39^a$ vanillic acid					Adom et al. (2003)
	$7.1–8.6^d$ GA					
	$1.06–1.42^d$ CAT					

^{a} [mg.kg^{-1}], ^{b} [mg. kg^{-1} DM], ^{c} [mmol.kg^{-1}], ^{d} [mmol.kg^{-1}], TP – total polyphenols, PA – phenolic acids, CRP – catechin, resorcin and phloroglucinol, GA – gallic acid equivalents, CAT – catechin equivalents

2001). Z h o u et al. (2005) detected significant levels of phenolic acids, tocopherols and carotenoids as antioxidants of hard red winter wheat bran. Buckwheat seeds also contain 0.2 mg.kg^{-1} selenium, corn 0.5 mg.kg^{-1} (D u k e, 1992).

Factors affecting antioxidant content in cereals

Environmental conditions (year, growing site) influence both, main nutrients as well as secondary minor antioxidants, e.g. polyphenols (L a c h m a n et al., 1998). Positive correlations were detected between antioxidant activity and either total solar radiation ($r = 0.97$, $p = 0.03$) or average daily solar radiation (Z h o u, Y u, 2004). Significant differences between oat cultivars and antioxidant activity and phenolics and growing localities were found by E m m o n s and P e t e r s o n (2001). On contrary, L i a n g l i and Z h o u (2004) did not find any correlation between solar radiations and antioxidant properties of bran extracts from Platte wheat grown at different locations suggesting that a selected wheat genotype may respond to the environmental changes differently. In other study (L i a n g l i et al., 2004) no significant correlation between total solar radiation, daily average solar radiation and hours exceeding temperature 32 °C in three winter wheat varieties was recorded, but the authors conclude that both, variety and growing location might significantly alter the antioxidant properties and the total phenolic contents of wheat flour. As D i m b e r g et al. (2005) reported, hydroxycinnamic acids showed cultivar and year differences in oat (*Avena sativa* L.) grains, but were not influenced significantly by nitrogen rates or the cropping system. The results of A d o m et al. (2003) of eleven investigated wheat varieties showed that while total phenolic content, total antioxidant activity, and total flavonoid content did not vary greatly, on contrary significant differences of total ferulic acid content ($p < 0.05$) and carotenoid content ($p < 0.05$) were estimated. Carotenoid content in wheat varieties exhibited 5-fold, 3-fold, and 12-fold differences in lutein, zeaxanthin, and β-cryptoxanthin, resp. As M o u r e et al. (2001) recorded, the extraction yield and the antioxidant activity differed significantly in fractions of the milled durum wheat bran (bran, head shorts, tail shorts, low-quality flour and low-grade flour), but slight and insignificant differences were found among varieties. Solvent extracts of roasted wheat germ, which is an actual waste stream of wheat processing, have good antioxidant activity, when compared with some roasted foods (K r i n g s, B e r g e r, 2001) and they retard the autooxidation of corn oil and improve its storability (K r i n g s et al., 2000). After heating, natural antioxidants isolated from bran of cereals with addition of phytic acid could be suitable for lipid stabilisation and oil storage. P o k o r n ý et al. (2004) found that also natural amino acids such as methionine and cystine and phospholipids as components contained in breakfast cereals could exert as active antioxidants. As H o l a s o v á et al. (2001) by comparison of antioxidant activity of oat, barley and buckwheat estimated, antioxidant activity increased in ascending sequence: oat < barley < buckwheat. Protective factors from buckwheat haulm, hulls, seeds, dehulled seeds were as high as 1.1; 1.5; 2.2; 2.6 and 4.1. Protective factors increased with higher number of leaves. Also when biscuits with addition of buckwheat leaves were prepared, antioxidant activity increased with higher proportion of leaves (addition of 15% of leaves increased antioxidant activity to 1.6). Because phenolic antioxidants are concentrated mainly in bran, enriched fractions with higher antioxidant activity levels could be obtained using dry milling and sieving, as it was shown by Gray et al. (2000) in oats.

CONCLUSION

Several studies have shown a consistent protective role of cereals consumption in reduced risk of coronary heart disease and reduced mortality. Since most cereal phenolics occur in the outer layers of grains, whole grains and enriched fractions are recommended for optimal health. Complex of polyphenolics, tocotrienols and tocopherols and carotenoids contained in cereals produced important antioxidant complex with beneficial effects on human health. The aim of future trend is to enhance levels of these antioxidants and to reach higher nutritional values of cereals by breeding of improved varieties and selection of optimal growing conditions.

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LACHMAN, J. – CAPOUCHOVÁ, I. (Česká zemědělská univerzita, Fakulta agrobiologie, potravinových a přírodních zdrojů, katedra chemie, katedra rostlinné výroby, Praha, Česká republika):

Složení a příspěvek komplexu antioxidantů vybraných obilovin k jejich nutriční kvalitě.

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Obiloviny jsou uznávány jako dobrý zdroj antioxidantů přispívajících ke zlepšení zdravotního stavu – fenolů, tokoferolů a karotenoidů. Hlavními antioxidanty obsaženými v obilovinách jsou polyfenolické sloučeniny, zvl. fenolkarboxylové kyseliny, kumariny, flavonoidy a anthokyany. V článku je diskutována antioxidační aktivita ve vztahu ke kvalitativnímu a kvantitativnímu složení dominantních antioxidantů, zvl. fenolických látek, v obilovinách a vliv odrůd a pěstebních podmínek na jejich obsah. Rovněž je uveden přehled rozdílů mezi jednotlivými vybranými obilovinami ve složení a obsahu různých antioxidantů.

antioxidanty obilovin; polyfenoly; tokoferoly; karotenoidy

Contact Address:

Prof. Ing. Jaromír L a c h m a n , CSc., Česká zemědělská univerzita v Praze, 165 21 Praha 6-Suchdol, Česká republika, tel.: + 420 224 382 717, fax: + 420 234 381 840, e-mail: lachman@af.czu.cz